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(54) **Releasably encapsulated active substrates**

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Description

The present invention relates to active substrates such as bleach activators releasably encapsulated in a coating thereon and methods of applying the same.

It is well known to use bleaches and bleach activators in detergent formulations. One of the important aspects of such formulations is that they should be capable of being stored over a significantly long period both by the producers of such formulations, the retailers of the product and by the end user, e.g. the housewife, who usually buys in bulk and likes to use it in small aliquots for washing as and when necessary. However, it is also well recognised that the components of such formulations, especially the bleaches and bleach activators, have an unacceptably short storage life due to their tendency to undergo undesirable physical or chemical changes, thereby resulting in deterioration of the formulation which may manifest itself as, e.g. loss of activity, discolouration, loss of attrition resistance, hygroscopicity and hence caking by absorption of moisture, staining the clothes washed or as malodour. It has been found that the bleaches and bleach activators in particular are prone to such undesirable changes.

It has been known to apply protective barrier coatings on relatively unstable compounds to improve their storage stability. Catalysts used in chemical reactions are a well known example where barrier coatings have been applied.

Peroxy compounds for use in bleaching formulations are protected with barrier coatings comprising metal salts, for example in US-A-4105827 and FR-A-2229768. Bleach activators of various types are encapsulated in metal salt protective coatings in EP-A-174132 and CA-A-0676777.

In the case of active substrates such as bleach activators there is the added problem that any coating applied should be such that:

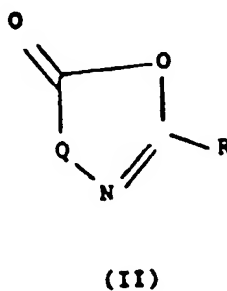
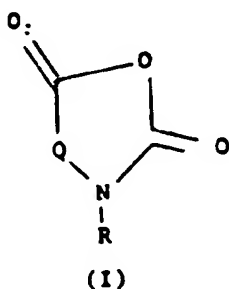
- (a) the active species is readily released when in contact with the aqueous wash system,
- (b) it mitigates any problems of dye damage or staining by the use of a bleach activator
- (c) the barrier coating itself should not interfere with the other components in the formulation,
- (d) the barrier coating does not adversely affect the wash or the clothes being washed in terms of causing dye damage or staining, and
- (e) should be user friendly and friendly towards the environment when discarded with the wash water.

It has now been found that the relative instability of active substrates such as bleach activators or the risk of dye damage or staining thereby can be mitigated by encapsulating the substrate in its powder or granular form in a barrier coating capable of releasing the active substrate in the aqueous wash system without adversely affecting the clothes being washed, the user or the environment.

Accordingly, the present invention relates to a process for encapsulating a bleach activator comprising the steps of:

- i) forming a composite particulate substrate having particle size in the range 200-2000 μm consisting of the bleach activator and binder and optionally containing disintegrating aid, surfactant and/or filler,
- ii) coating the composite particulate substrate with a solution of a metal salt of an inorganic acid, which is soluble in water to the extent of at least 3 g per 100 g at 15°C, and
- iii) drying the coated particles.

The process is of particular benefit for encapsulating cyclic anhydride activators of the formula I and lactones of the formula II and in the process the activator preferably comprises at least one compound selected from a cyclic anhydride of the structural formula (I) or a lactone of the structural formula (II) below:



wherein Q is a divalent organic grouping such that Q and N together with the carbonyl and oxygen functions form one or more cyclic structures and in (I) R is H, an alkyl, aryl, halogen, a carboxylic or a carbonyl containing function, and in (II) R is a C₂ or higher alkyl, alkaryl, aryl, aralkyl, alkoxyl, haloalkyl, amino, amino alkyl, dialkyl amino, carboxylic or a carbonyl-containing function.

By the term "active substrate" as used herein and throughout the specification is meant a bleach activator as such or a composite which comprises such bleach activator and one or more other components including conventional binders such as e.g. a bentonite clay; surfactants such as polyoxyalkylene sorbitan oleate esters, e.g. Tween (Registered Trade Mark) an alkali metal salt of a polycarboxylic acid, e.g. Displex-G40 (Registered Trade Mark, ex Allied Colloids, UK); disintegrating aids such as cross-linked carboxy methyl cellulose derivatives e.g. Ac-di-sol (Registered Trade Mark) or a polyacrylate; and fillers such as the cellulosic type, e.g. Avicel (Registered Trade Mark).

Bleach activators of formula (I) are claimed and described in our published EP-A-331300 and those of formula (II) are claimed and described in our published EP-A-332294 and are incorporated herein by reference.

In particular, such compounds include bleach activators such as 2-hydrocarbyl (4H) 3,1-benzoxazin-4-ones (especially the 2-methyl and 2-aryl derivatives), the 2-N,N-dialkylamino (4H) 3,1-benzoxazin-4-ones (especially the 2-N,N-dimethyl derivative) and isatoic anhydride and its homologues and derivatives. Bleach activators described in published EP-A-170386 (N-alkoyl-6-aminoperoxycarboxylic acids and their salts) and in GB-A-2832021 (tetraacetyl ethylene diamine) can also be encapsulated in a coating to improve their stability and are incorporated herein by reference.

The term "aqueous medium" as used herein and throughout the specification is meant to include the aqueous alkaline medium encountered in a wash cycle or during a washing procedure.

The metal salts of inorganic acids which can be used to form the encapsulating coating must be soluble in the aqueous medium although it would be advantageous if they are soluble in water. The solubility should preferably be at least 3g/100g of the aqueous medium at ambient temperatures, eg 15°C, although the greater the solubility, the better. Examples of such compounds include the water soluble carbonates, sulphates and phosphates of the metals in Groups I-III of the Periodic Table, especially the alkali metals, some alkaline earth metals such as magnesium, zinc and Group III metals such as aluminium. Particularly preferred are the sulphates and phosphates of sodium, potassium, zinc and aluminium. Whichever metal salt is chosen, the salt should be such that it is capable of forming an encapsulating barrier coating on the active substrate.

In the case of some compounds of the structure type (II), especially if the compound is a 2-aryl substituted benzoxazin-4-one, such activators cause dye damage. The performance of such activators can be improved by using an encapsulating coating of a zinc salt such as zinc sulphate. On the other hand, with activators of the type (I) ie those having an isatoic anhydride type structure, the problems of staining and dye damage can be mitigated by using an encapsulating coating of an aluminium salt such as aluminium sulphate.

The encapsulating coating should suitably form a minor proportion of the encapsulated product. That is, the active substrate should be at least 50% w/w of the encapsulated product, preferably greater than 65% w/w of the encapsulated product and most preferably from 65-80% w/w.

Ideally, the thickness of the coating encapsulating the active substrate is suitably such that it does not peel off or is not readily removed by attrition and is preferably at least 0.03 micrometers.

The encapsulation should however be such that it completely covers the active substrate coated. The active substrate is suitably in the form of a powder or granules prior to encapsulation. The initial particle size of the substrate should be preferably from 50-200 micrometers for the powder and from 200-2000 micrometers for the granules. Substrates having particle sizes within this range can be produced from commercially available material by milling and/or grinding, granulation or preferably by the technique of extrusion and spheronisation. In producing the powder or granules of the active substrate they may be in the form of a composite comprising the bleach activator, binders, dispersing aids, surfactants and fillers as described above. The encapsulating coating can be applied on the substrate by conventional means. It is preferable to create a fluidised bed of the substrate particles and to spray them with a solution of the metal salt. In using this technique the conditions should be controlled carefully in order to achieve satisfactory encapsulation. For instance, the fluidisation of the substrate particles should be such that they float in the fluidising medium as separate and distinct particles for a sufficiently long time in the coating environment so as to enable the spray of the metal salt to substantially completely encapsulate and hermetically seal substantially all of the particles individually. At the same time the residence time within the coating environment and the temperature within the coating environment should be such that before the encapsulated particles emerge from the environment they are substantially dry and resistant to (a) loss of coating

by attrition and (b) agglomeration. In this context the choice of a fluidising medium is also important in that it should be substantially inert to the encapsulating process and should not adversely affect the nature of the substrate being encapsulated or the encapsulating coating. An example of a suitable fluidising medium is air.

The present invention is further illustrated with reference to the following Example.

Example 1

In the Example below the following components were used in a formulation to produce the active substrate:

| | |
|--------------------------------------|---------|
| Isatoic anhydride (bleach activator) | 80% w/w |
| Bentonite clay (binder) | 9% w/w |
| Ac-di-sol* (disintegrating aid) | 2% w/w |
| Avicel* (a cellulosic filler) | 9% w/w |

* Registered Trade Mark

The above components were formed into a dough in water and subjected to extrusion followed by spheronisation to obtain granules having a particle size of 500-1000 micrometers.

The granules were then fluidised in a Strea-1 fluidiser at a spray rate of about 6g/min through two-fluid nozzle with atomising air pressure of about 0.8 bar.

Air was used as the fluidising medium at an air volume of 10 units on Strea 1. The inlet air temperature was 48°C and the outlet air temperature was 36°C.

A solution of 150g of anhydrous sodium sulphate in 700g of water was used as the encapsulating solution.

This sodium sulphate solution was sprayed in a direction cocurrent with the fluidising air using a Wurster column. The spraying of the solution took about 1.5 hours to encapsulate the granules. The encapsulated granules were then dried for a further 20 minutes during which time the temperature was increased to 52°C at the inlet and 46°C at the outlet to bake the encapsulating coating into a solid, dry barrier.

The encapsulated granules so produced were mixed at a concentration of 5% w/w with a detergent powder containing 80% w/w ECE Base (ex Westlairs Limited, North Green, Datchet, Slough SL3 9JH, Berkshire, UK) and 15% w/w of a perborate bleach and stored in open packs at 37°C and 70% relative humidity. The resultant detergent formulation did not suffer any discolouration or substantial loss of activity after storage for 2 months.

That the solubility of the coating in the aqueous medium is unaffected is illustrated by a comparison of coated and uncoated spheres made with the above formulation where it can be seen that there is no significant difference between whole and crushed spheres:

Test conditions : 40°C, 2.5% active isatoic anhydride (hereafter "IA") was used in detergent base containing sodium perborate tetrahydrate. Washes were carried out in a Tergo-tometer over a period of 20 minutes. 5.85g of detergent base plus 0.15g of bleach activator at 100% active were used i.e. 0.3g of formulated isatoic anhydride spheres.

Substrate Cloths: EMPA 114 Red wine stain and WPK BC-1 tea stain

Measurements : Reflectance measurements were taken with ICS-Texicon Micromatch spectrometer. Results are expressed as percentage stain removal (%SR) calculated from the following expression:

$$\%SR = \frac{L(\text{final}) - L(\text{initial})}{L(\text{standard}) - L(\text{final})} \times 100$$

L(final) = final reflectance value
L(initial) = initial reflectance value
L(standard) = standard reflectance value

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L value is reflectance value as defined in Committee Internationale D'Eclairage LAB system (CIELAB).

| | FORM | L _{SR} | |
|------------------------------------|---|-----------------|-------|
| | | EMPA | TEA |
| Isatoic Anhydride (ex BASF) | | 70.09 | 29.52 |
| whole spheres as per formulation | Coated with Na ₂ SO ₄ 50% active in IA | 69.37 | 28.78 |
| crushed spheres as per formulation | " " " | 69.58 | 28.91 |
| Tetra Acetyl Ethylene Diamine | (Pure, ex Warwick Int.) | 66.84 | 22.07 |
| Blank | Detergent base alone | 60.99 | 13.04 |
| Isatoic Anhydride | 53-106 micrometers | 69.21 | 28.35 |
| least significant difference) | | 1.22 | |

Example 2

Granules containing 80% isatoic anhydride bleach activator were encapsulated with the inorganic salts detailed below. These coated granules (20 parts) were mixed with a phosphate-free detergent base which contained 25% sodium perborate monohydrate (80 parts). Samples from the detergent formulations thus prepared were then spread in narrow strips of ca. 2cm width onto a test cloth of white cotton (EMPA 221). This cloth had previously been placed in a tray and dampened with sufficient water to absorb into and dampen the strips of detergent formulation. After 30 minutes the cotton test cloth was thoroughly rinsed in running tap water and air dried.

The above test was repeated a further three times. A panel of five observers was then used to compare the extent of brown staining of the cotton cloths under artificial daylight (D65) illumination in an ICS-Texicon light cabinet. Each observer was asked to score the staining underneath the detergent strips on a scale of 1 to 5 where:- cloth(s) with least staining = 1, and cloth(s) with most staining = 5.

The marks obtained are given below.

| Formulation containing bleach activator encapsulated with; | Mean score |
|--|------------|
| Zinc sulphate heptahydrate (ca. 38% w/w) | 1.10 |
| Zinc sulphate heptahydrate (ca. 31% w/w) | 1.40 |
| Zinc sulphate heptahydrate (ca. 25% w/w) | 1.65 |
| Aluminium sulphate hexadecahydrate (ca. 38% w/w) | 2.05 |
| Aluminium sulphate hexadecahydrate (ca. 31% w/w) | 2.45 |
| Aluminium sulphate hexadecahydrate (ca. 25% w/w) | 3.40 |
| Sodium acetate (ca. 38% w/w) | 5.00 |

The results show that the bleach activator granules encapsulated with the zinc and aluminium salts exhibit significantly reduced tendency for staining of the test fabric than those encapsulated with a salt of an organic acid.

Example 3

Granules containing 82% 2-phenyl benzoxazine-4-one (2PB4) bleach activator were encapsulated with the inorganic salts detailed below. These coated granules (20 parts) were mixed with a phosphate-free detergent base which contained 25% sodium perborate monohydrate (80 parts). Samples from the detergent formulations thus prepared were then spread in narrow strips of ca. 2cm width onto a test cloth of cotton dyed with immedial black (EMPA 115). This cloth had previously been placed in a tray and

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dampened with sufficient water to absorb into and dampen the strips of detergent formulation. After 30 minutes the cotton test cloth was thoroughly rinsed in running tap water and air dried. The above test was repeated.

Reflectance measurements were taken with an ICS-TEXCON Micromatch Spectrometer. The average results from 10 readings from underneath each test strip on each test cloth are expressed as percentage stain removal (%SR).

Composition of 2PB4 granules:-

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| | |
|----------------|---------|
| 2PB4 | 82% w/w |
| Bentonite clay | 13% w/w |
| Dispex G40 | 2% w/w |
| Avicel | 3% w/w |

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| Formulation containing 2PB4 bleach activator encapsulated with; | %SR |
|---|------|
| Aluminium sulphate (ca. 38% w/w coating) | 14.4 |
| Zinc sulphate (ca. 38% w/w coating) | 13.7 |
| Uncoated granules | 27.6 |

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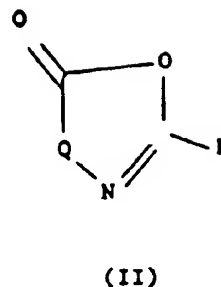
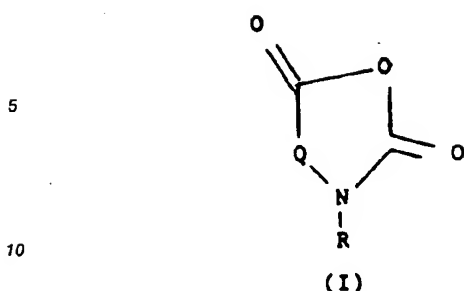
Visual observations confirmed the marked reduction of 'pinholing' dye damage for the zinc and aluminium sulphate coated granules when compared with uncoated granules.

The results show that the bleach activator granules encapsulated with the zinc and aluminium salts exhibit significantly reduced tendency for dye damage.

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Claims

1. A process for encapsulating a bleach activator comprising the steps of:
 - i) forming a composite particulate substrate having particle size in the range 200-2000 μm consisting of the bleach activator and binder and optionally containing disintegrating aid, surfactant and/or filler,
 - ii) coating the composite particulate substrate with a solution of a metal salt of an inorganic acid, which is soluble in water to the extent of at least 3 g per 100 g at 15 °C, and
 - iii) drying the coated particles.
2. A process according to claim 1 in which the composite particulate substrate is suspended in air in a fluidised bed during the coating step.
3. A process according to any preceding claim in which the metal salt is applied in a dye-damage-inhibiting and/or fabric staining-inhibiting amount.
4. A process according to claim 3 in which the thickness of the salt coating of the product is at least 0.03 μm .
5. A process according to any preceding claim in which the metal of the metal salt is selected from alkali metals, alkaline earth metals, zinc and group III metals.
6. A process according to claim 5, in which the metal salt is a salt of zinc or aluminium.
7. A process according to claim 6, in which the metal salt is selected from zinc sulphate and aluminium sulphate.
8. A process according to any preceding claim in which the encapsulated activator is incorporated into a powder detergent containing a peroxygen bleach source.
9. A process according to any preceding claim in which the activator is at least one compound selected from a cyclic anhydride of the structural formula I or a lactone of the structural formula II below



- 15 wherein Q is a divalent organic grouping such that Q and N together with the carbonyl and oxygen functions form one or more cyclic structures and in (I) R is H, an alkyl, aryl, halogen, a carboxylic or a carbonyl containing function, and in (II) R is a C₂ or higher alkyl, alkaryl, aryl, aralkyl, alkoxy, haloalkyl, amino, aminoalkyl, dialkyl amino, carboxylic or a carbonyl containing function.
- 20 10. A process according to claim 9 in which the bleach activator is selected from a 2-hydrocarbyl (4H) 3,1-benzoxazin-4-one, 2-aryl (4H) 3,1-benzoxazin-4-one, 2-N,N-dialkylamino (4H) 3,1-benzoxazin-4-one and isatoic anhydride.
- 25 11. A process according to any preceding claim in which the binder is a bentonite clay, the surfactant is a polyoxyalkylene sorbitan oleate ester or an alkali metal salt of a polycarboxylic acid, the disintegrating aid is a cross-linked hydroxymethyl cellulose derivative and the filler is a cellulosic filler type.

Patentansprüche

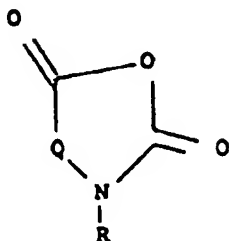
- 30 1. Verfahren zur Verkapselung eines Bleichaktivators, umfassend die folgenden Schritte:
- i) Bilden eines teilchenförmigen Kompositsubstrats mit einer Teilchengröße im Bereich von 200-2000 µm, das aus dem Bleichaktivator und einem Bindemittel besteht und gegebenenfalls ein Zerfallshilfsmittel, ein Tensid und/oder einen Füllstoff enthält,
 - ii) Beschichten des teilchenförmigen Kompositsubstrats mit einer Lösung eines Metallsalzes einer anorganischen Säure, die in Wasser bis zu einem Grad von mindestens 3 g pro 100 g bei 15 °C löslich ist, und
 - iii) Trocknen der beschichteten Teilchen.
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- 40 2. Verfahren nach Anspruch 1, bei welchem das teilchenförmige Kompositsubstrat während des Beschichtungsschrittes in einem Fließbett in Luft suspendiert ist.
3. Verfahren nach irgendeinem vorhergehenden Anspruch, bei welchem das Metallsalz in einer eine Schädigung der Farbe und/oder eine Verschmutzung des Gewebes hemmenden Menge verwendet wird.
- 45 4. Verfahren nach Anspruch 3, bei welchem die Dicke der Salzschrift des Produkts mindestens 0,03 µm beträgt.
5. Verfahren nach irgendeinem vorhergehenden Anspruch, bei welchem das Metall des Metallsalzes aus Alkalimetallen, Erdalkalimetallen, Zink und Metallen der Gruppe III ausgewählt ist.
- 50 6. Verfahren nach Anspruch 5, bei welchem das Metallsalz ein Zink- oder Aluminiumsalz ist.
7. Verfahren nach Anspruch 6, bei welchem das Metallsalz aus Zinksulfat und Aluminiumsulfat ausgewählt ist.
- 55 8. Verfahren nach irgendeinem vorhergehenden Anspruch, bei welchem der verkapselte Aktivator in ein Waschpulver eingebracht wird, das eine Peroxid-Bleichquelle enthält.

9. Verfahren nach irgendeinem vorhergehenden Anspruch, bei welchem der Aktivator mindestens eine aus einem cyclischen Anhydrid der Strukturformel I oder einem Lacton der Strukturformel II unten ausgewählte Verbindung ist

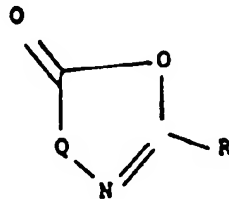
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(I)



(II)

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worin Q eine zweiwertige organische Gruppe ist, so daß Q und N zusammen mit den Carbonyl- und Sauerstoff-Funktionen eine oder mehrere cyclische Strukturen bilden, und R in (I) H, eine Alkyl-, Aryl-, Halogen-, eine Carboxyl- oder eine Carbonyl-haltige Funktion ist und R in (II) eine C₂- oder eine höhere Alkyl-, Alkaryl-, Aryl-, Aralkyl-, Alkoxy-, Halogenalkyl-, Amino-, Aminoalkyl-, Dialkylamino-, Carboxyl- oder eine Carbonyl-haltige Funktion ist.

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10. Verfahren nach Anspruch 9, bei welchem der Bleichaktivator aus einem 2-Hydrocarbyl-(4H)-3,1-benzoxazin-4-on, 2-Aryl-(4H)-3,1-benzoxazin-4-on, 2-N,N-Dialkylamino-(4H)-3,1-benzoxazin-4-on und Isatosäureanhydrid ausgewählt ist.

11. Verfahren nach irgendeinem vorhergehenden Anspruch, bei welchem das Bindemittel eine Bentonit-Tonerde, das Tensid ein Polyoxyalkylensorbitanoleat-Ester oder ein Alkalimetallsalz einer Polycarbonsäure, das Zerfallshilfsmittel ein vernetztes Hydroxymethyl-cellulose-Derivat und der Füllstoff ein Füllstoff vom Cellulose-Typ ist.

Revendications

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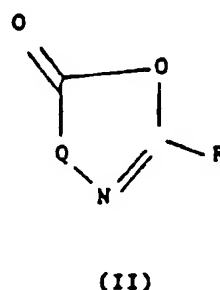
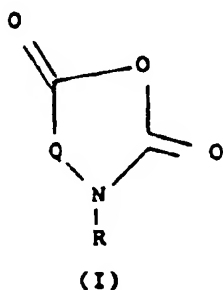
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1. Procédé d'encapsulation d'un activateur de blanchiment comprenant les étapes consistant à :
 - i) former un substrat particulaire composite présentant une dimension de particules comprise dans la gamme de 200 à 2 000 μm , constitué de l'activateur de blanchiment et d'un liant et contenant éventuellement un adjuvant de délitement, un agent tensioactif et/ou une charge,
 - ii) revêtir le substrat particulaire composite d'une solution d'un sel métallique d'un acide inorganique, lequel est soluble dans l'eau jusqu'à au moins 3 g pour 100 g à 15 °C et
 - iii) sécher les particules revêtues.
2. Procédé selon la revendication 1, dans lequel on met le substrat particulaire composite dans l'air dans un lit fluidisé lors de l'étape de revêtement.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel on applique le sel métallique en une quantité inhibant la détérioration de la teinture et/ou inhibant la souillure de l'étoffe.
4. Procédé selon la revendication 3, dans lequel l'épaisseur du revêtement de sel du produit est d'au moins 0,03 μm .
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel on choisit le métal du sel métallique parmi les métaux alcalins, les métaux alcalino-terreux, le zinc et les métaux du groupe III.
6. Procédé selon la revendication 5, dans lequel le sel métallique est un sel de zinc ou d'aluminium.
7. Procédé selon la revendication 6, dans lequel on choisit le sel métallique parmi le sulfate de zinc et le sulfate d'aluminium.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel on incorpore l'activateur encapsulé dans un détergent en poudre contenant une source peroxygénée de blanchiment.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'activateur est au moins un composé choisi parmi un anhydride cyclique de formule développée I et une lactone de formule développée II ci-dessous



dans lesquelles Q représente un groupement organique divalent de sorte que Q et N, avec les fonctions carbonyle et oxygène, forment une ou plusieurs structures cycliques et, dans (I), R représente H, une fonction alkyle, aryle, halogène, carboxylique ou contenant un carbonyle et, dans (II), R représente une fonction alkyle en C₂ ou plus, alcaryle, aryle, aralkyle, alcoyle, halogénoalkyle, amino, aminoalkyle, dialkylamino, carboxylique ou contenant un carbonyle.

10. Procédé selon la revendication 9, dans lequel on choisit l'activateur de blanchiment parmi une 2-hydrocarbonyl (4H) 3,1-benzoxazin-4-one, une 2-aryl (4H) 3,1-benzoxazin-4-one, une 2-N,N-dialkylamino (4H) 3,1-benzoxazin-4-one et l'anhydride isatoïque.
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le liant est l'argile bentonite, l'agent tensioactif est un ester oléate de polyoxyalkylènesorbitane ou un sel de métal alcalin d'un acide polycarboxylique, l'adjuvant de délitement est un dérivé d'hydroxyméthylcellulose réticulé et la charge est du type charge cellulosique.